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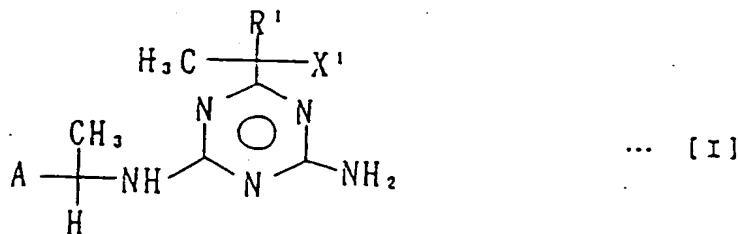
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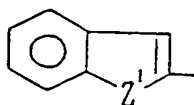
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1280, Kamiizumi, Sodegaura-machi Kimitsu-gun, Chiba-ken(JP)Inventor: **Kobayashi, Izumi, c/o Idemitsu Kosan Co.Ltd.****1-1, Marunouchi 3-chome, Chiyoda-ku, Tokyo(JP)**Inventor: **Kikkawa, Nobuyuki, c/o Idemitsu Kosan Co.Ltd.****1280, Kamiizumi, Sodegaura-machi Kimitsu-gun, Chiba-ken(JP)**Inventor: **Takematsu, Tetsuo****612, Mine-machi Utsunomiya-shi, Tochigi-ken(JP)**(74) Representative: **Türk, Gille, Hrabal Brucknerstrasse 20 W-4000 Düsseldorf 13(DE)**(54) **Herbicidal compositions.**

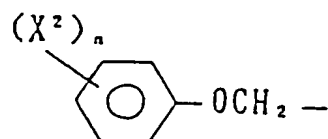
(57) A synergistic herbicidal composition comprising as active ingredients triazine derivatives represented by general formula [I]:



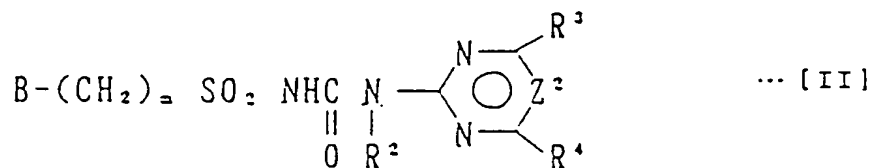
[wherein A represents



(wherein Z represents oxygen atom or sulfur atom), or



wherein X^2 represents methyl group or fluorine atom and n represents 0 or an integer of 1 or 2; R^1 represents hydrogen atom or methyl group; and X^1 represents fluorine atom or chlorine atom] and sulfonylurea type herbicide represented by general formula [II]:



BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

5 The present invention relates to a herbicidal composition comprising triazine derivatives and sulfonylurea type herbicides as active ingredients.

STATEMENT OF THE PRIOR ART

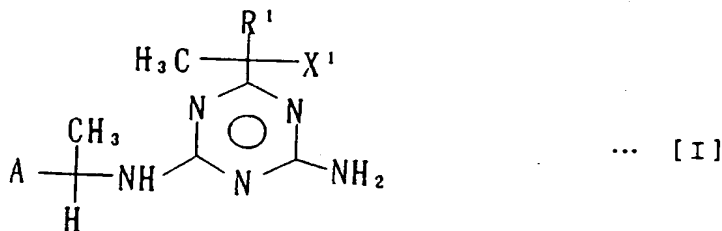
10 Heretofore a variety of herbicides have been developed and have contributed to agricultural productivity and saving labors. However, some herbicides have been used over many years and hence, weeds which are insufficiently controlled are increasing. It has thus been desired to develop herbicides having a wide range of herbicidal spectrum and those effective also against such troublesome weeds. Also in order to remove environmental pollution problems caused by conventional herbicides, it has been desired to
 15 develop herbicides having a high activity at a low dosage. Moreover, in order to control weeds emerging non-uniformly over a long period of time, it has been desired to develop herbicides having an excellent residual activities and having flexibility of treatment to exhibit effectiveness even though the treatment is performed over a long period from pre-emergence to a wide range of growing stage of weeds.

Under such a situation, the present inventors found that specific, novel triazine derivatives containing a
 20 halo alkyl are compounds which show a high herbicidal effect against troublesome weeds both by soil treatment and by foliage treatment, without causing any phytotoxicities of Gramineae field crops, and moreover provide an excellent effectiveness against weeds in paddy fields (Japanese Patent Application Nos. 1-38178 and 1-154465). The present inventors made extensive investigations to further improve the herbicidal activity of the triazine derivatives.

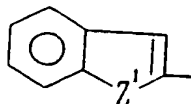
25 As a result, it has been found that a composition comprising the triazine derivatives in combination with specific sulfonylurea type herbicides exhibits excellent herbicidal activity which can be unexpected from each property of these herbicides and shows a high herbicidal effect at a low dosage and at the same time, has a wide range of herbicidal spectrum. The present invention has thus been accomplished.

30 SUMMARY OF THE INVENTION

That is, the present invention provides a herbicidal composition comprising as active ingredients triazine derivatives represented by general formula [I]:

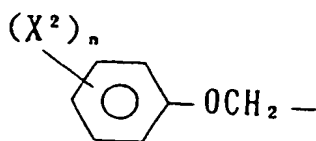


45 [wherein A represents

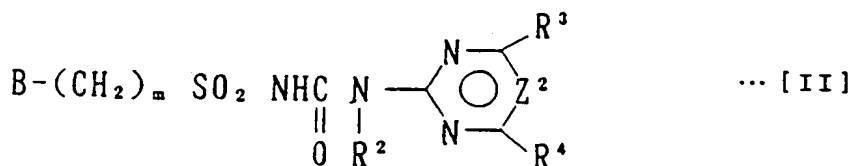


(wherein Z represents oxygen atom or sulfur atom), or

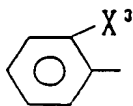
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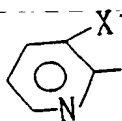
(wherein X^2 represents methyl group or fluorine atom and n represents 0 or an integer of 1 or 2); R^1 represents hydrogen atom or methyl group; and X^1 represents fluorine atom or chlorine atom) and
 10 sulfonyleurea type herbicide represented by general formula [II]:



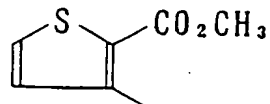
20 [wherein B represents



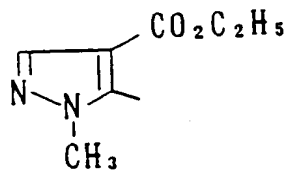
(wherein X^3 represents a chlorine atom, CO_2CH_3 , $\text{CO}_2\text{C}_2\text{H}_5$ or $\text{OCH}_2\text{CH}_2\text{Cl}$),



(wherein X^4 represents $\text{CON}(\text{CH}_3)_2$ or $\text{CO}_2\text{C}_2\text{H}_5$),



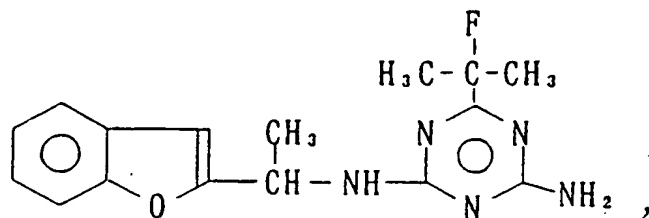
or



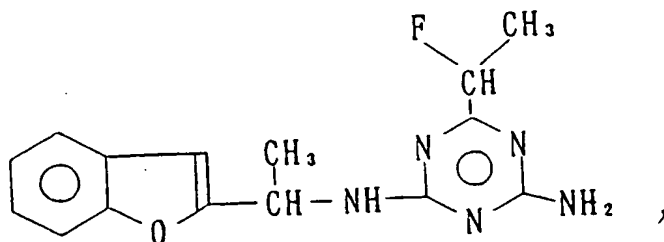
50 R^2 represents a hydrogen atom or methyl group, R^3 and R^4 each represents methyl group, OCH_3 or OCHF_2 , provided that R^3 and R^4 may be the same or different; Z^2 represents CH or a nitrogen atom, and m is 0 or 1].

DETAILED DESCRIPTION OF THE INVENTION

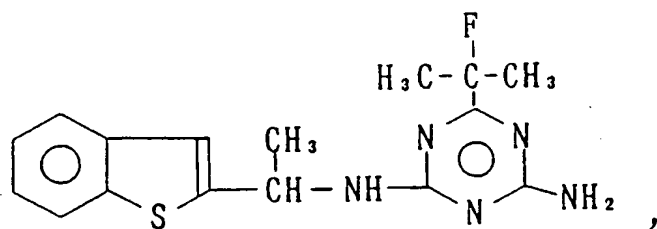
55 Specific examples of the triazine derivatives represented by general formula [I] described above include: 2-amino-4-[1-(benzofuran-2'-yl)ethylamino]-6-(α -fluoro, α -methylethyl)-s-triazine



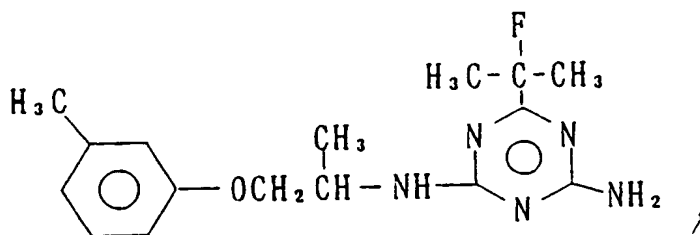
10 2-amino-4-[1-(benzofuran-2'-yl)ethylamino]-6-(α-fluoroethyl)-s-triazine



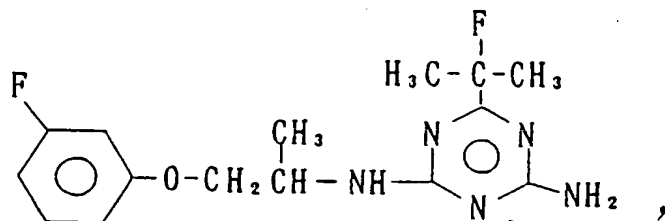
25 2-amino-4-[1-(benzothiophen-2'-yl)ethylamino]-6-(α-fluoro,α-methylethyl)-s-triazine



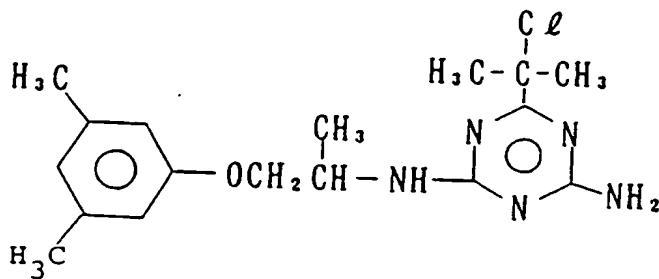
35 2-amino-4-(α-fluoro,α-methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine



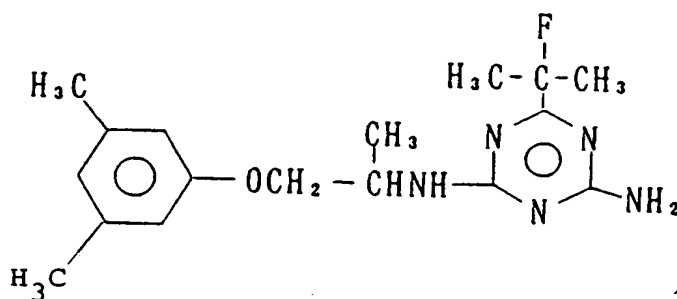
50 2-amino-4-(α-fluoro,α-methylethyl)-6-[2-(3-fluorophenoxy)-1-methylethylamino]-s-triazine



2-amino-4-(α -chloro, α -methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine

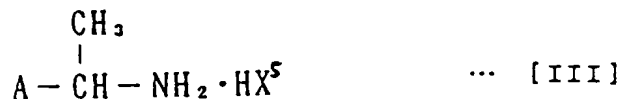


2-amino-4-(α -fluoro, α -methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine

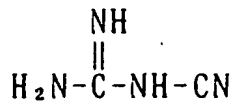


etc.

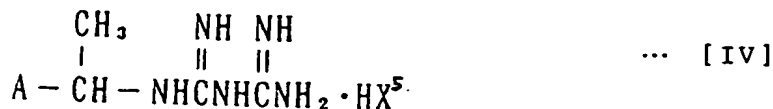
The triazine derivatives represented by general formula [I] described above may be prepared by various processes. Among these processes, an advantageous process comprises reacting alkyl amine salts represented by general formula [III]:



[wherein A has the same significance as described above and X^5 represents a halogen atom] with cyanoguanidine represented by the following formula



to prepare alkyl biguanide salts represented by general formula [IV]:



[wherein A and X^5 have the same significances as described above]; and then reacting the alkyl biguanide

salts with alkyl esters represented by general formula [V]:



[wherein R¹ and X¹ have the same significances as described above; and R⁵ represents an alkyl group having 1 to 4 carbon atom]. According to this process, the desired triazine derivatives represented by general formula [I] can be efficiently obtained by reacting the alkylamine salts represented by general formula [III] with cyanoguanidine to prepare the alkyl biguanide salts represented by general formula [IV], and then reacting the salts [IV] with the alkyl esters represented by general formula [V].

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Herein, in the reaction of the alkylamine salts represented by general formula [III] with cyanoguanidine, both compounds may be used in equimolar amounts. As a solvents, there may be used cyclic hydrocarbons such as benzene, decaline, alkylnaphthalenes, etc.; chlorinated hydrocarbons such as carbon tetrachloride, ethylene dichloride, chlorobenzene, dichlorobenzene, trichlorobenzene, etc. A reaction temperature is not particularly limited but the reaction sufficiently proceeds at a high temperature ranging from 80 to 200 °C.

According to this reaction, the alkylbiguanide derivative salts shown by general formula [IV] are obtained. By reacting [IV] with alkyl esters represented by general formula [V], the desired triazine derivatives represented by general formula [I] are prepared. This reaction efficiently proceeds generally in a solvent such as alcohols, e.g., methanol, ethanol, isopropanol, etc., various ketones, aliphatic hydrocarbons, various ethers, various cyclic hydrocarbons, chlorinated hydrocarbons, etc., in the presence of a catalyst such as a base, etc. at a temperature of about 10 to about 100 °C.

Optical isomers are also present in these compounds and the products are obtained generally in the racemic form. However, it is also possible to the respective enantiomers in a conventional manner such as asymmetric synthesis, etc. In the present invention, both racemic compounds and optical isomers alone may be used. In the present invention, the products may be in the form of salts with inorganic acid or organic acid.

On the other hand, specific examples of the sulfonylurea type herbicide represented by general formula [II] described above include 2-chloro-N-[4-methoxy-6-methyl-1,3,5-triazin-2-yl]-aminocarbonyl]-benzenesulfonamide, methyl 2-[[[4-methoxy-6-methyl-1,3,5-triazin-2-yl]-aminocarbonyl]-aminosulfonyl]-benzoate, methyl 2-[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-3-methylureidosulfonyl]benzoate, methyl 3-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]-aminosulfonyl]-2-thiophenecarboxylate, 3-(6-methoxy-4-methyl-1,3,5-triazin-2-yl)-1-[2-(2-chloroethoxy)-phenylsulfonyl]urea, methyl 2-[[[4,6-dimethylpyrimidin-2-yl] aminocarbonyl]-aminosulfonyl]benzoate, 2-[3-(4,6-bis(difluoromethoxy)-pyrimidin-2-yl)-ureidosulfonyl]benzoic acid methyl ester, 2-(4,6-dimethoxypyrimidin-2-ylcarbamoysulfamoyl)-N,N-dimethylnicotinamide, 1-(4,6-dimethoxypyrimidin-2-yl)-3-(ethylsulfonyl)-2-pyridinylsulfonylurea, methyl 2-[[[4,6-dimethoxypyrimidin-2-yl]aminocarbonyl]-aminosulfonyl]methyl]benzoate, ethyl 5-(4,6-dimethoxypyrimidin-2-ylcarbamoysulfamoyl)-1-methylpyrazol-4-carboxylate, etc. Among them, preferred are methyl 2-[[[4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]-aminosulfonyl]benzoate, methyl 3-[[[4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]-aminosulfonyl]-2-thiophenecarboxylate, 3-(6-methoxy-4-methyl-1,3,5-triazin-2-yl)-1-[2-(2-chloroethoxy)-phenylsulfonyl]urea, 2-[3-(4,6-bis(difluoromethoxy)-pyrimidin-2-yl)-ureidosulfonyl]benzoic acid methyl ester, 2-(4,6-dimethoxypyrimidin-2-ylcarbamoysulfamoyl)-N,N-dimethylnicotinamide, 1-(4,6-dimethoxypyrimidin-2-yl)-3-(ethylsulfonyl)-2-pyridinylsulfonylurea, methyl 2-[[[4,6-dimethoxypyrimidin-2-yl]aminocarbonyl]-aminosulfonyl]methyl]benzoate, and ethyl 5-(4,6-dimethoxypyrimidin-2-ylcarbamoysulfamoyl)-1-methylpyrazol-4-carboxylate.

Among the sulfonylurea type herbicides represented by general formula [II] described above, 2-(4,6-dimethoxypyrimidin-2-ylcarbamoysulfamoyl)-N,N-dimethylnicotinamide and 1-(4,6-dimethoxypyrimidin-2-yl)-3-(ethylsulfonyl)-2-pyridinylsulfonylurea can be prepared by the processes described in Japanese Patent Application Laid-Open No. 62-178588 and Japanese National Patent Application Laid-Open No. 2-500912, respectively. The other sulfonylurea type herbicides can be obtained by known processes. These sul-

fonylurea type herbicides have a wide spectrum for broad-leaved weeds or Gramineae weeds and are used for Gramineae crops such as wheat, barley, corn, sorghum, paddy rice plant, etc.

The herbicidal composition of the present invention comprises as active ingredients the triazine derivatives represented by general formula [I] described above and the sulfonylurea type herbicides represented by general formula [II] described above. A proportion of these components to be formulated is not particularly limited but in a wide range of proportion, an excellent synergistic effect can be obtained. In general, it is preferred to formulate the triazine derivative and the sulfonylurea type herbicide in a range of from 1000 : 1 to 1 : 100 (weight ratio).

The herbicidal composition of the present invention may be used in the form of wettable powders, emulsifiable concentrates, dusts, granules, flowable concentrates, solutions, etc., by blending the triazine derivatives represented by general formula [I] described above and the sulfonylurea type herbicides represented by general formula [II] described above with liquid carriers such as solvents, etc. or with solid carriers such as mineral powders, etc. In preparing into these forms, there may be added surfactants such as emulsifiers, dispersing agents, developers, suspending agents, permeating agents, stabilizers, etc. and, if necessary, other auxiliary agents.

Where the herbicidal composition of the present invention is used in the form of wettable powders, 10 to 55 wt% of the aforesaid triazine derivatives and the sulfonylurea type herbicide as active ingredients, 40 to 88 wt% of the solid carrier and 2 to 5 wt% of the surfactant may generally be formulated to prepare a composition and the composition may be used. Where the herbicidal composition is used in the form of emulsifiable concentrate or flowable concentrate, 5 to 50 wt% of the aforesaid triazine derivatives and the sulfonylurea type herbicide as active ingredients, 35 to 90 wt% of the solvent and 5 to 15 wt% of the surfactant and other auxiliary agent may generally be formulated to prepare a composition and the resulting composition may be used.

Where herbicidal composition is used in the form of dust, 1 to 15 wt% of the aforesaid triazine derivatives and the sulfonylurea type herbicide as active ingredients and 85 to 99 wt% of the solid carrier may generally be formulated to prepare a composition. Where the herbicidal composition of the present invention is used in the form of granules, 0.1 to 15 wt% of the aforesaid triazine derivatives and the sulfonylurea type herbicide as active ingredients, 80 to 97.9 wt% of the solid carrier and 2 to 5 wt% of the surfactant may generally be formulated to prepare a composition. Herein, as the solid carrier, finely divided mineral powders are used. As the finely divided mineral powders, there are diatomaceous earth, oxides such as slaked lime, etc.; phosphates such as apatite, etc.; sulfates such as gypsum, etc.; silicates such as talc, pyrophyllite, clay, kaolin, bentonite, acid-clay, white-carbon, quartz powders, silica powders, etc.

As the liquid carrier, there may be organic solvents, for example, paraffin type or naphthene type hydrocarbons such as kerosene, mineral oil, spindle oil, etc.; aromatic hydrocarbons such as benzene, toluene, xylene, etc.; chlorinated hydrocarbons such as o-chlorotoluene, trichloromethane, trichloroethylene, etc.; alcohols such as cyclohexanol, amyl alcohol, ethylene glycol, etc.; alcohol ethers such as ethylene glycol monomethyl ether, ethyleneglycol monoethyl ether, etc.; ketones such as isophorone, cyclohexanone, cyclohexenyl-cyclohexanone, etc.; ethers such as butyl cellosolve, dimethyl ether, methyl ethyl ether, etc.; esters such as isopropyl acetate, benzyl acetate, methyl phthalate, etc.; amides such as dimethylformamide, etc.; nitriles such as acetonitrile, propionitrile, etc.; sulfoxides such as dimethylsulfoxide, etc.; or a mixture thereof; or water and the like.

As the surfactant, there may be used any of anion type (alkylbenzene sulfonate, alkyl sulfonates, lauramide sulfonate, etc.), nonion type (polyoxyethylene octyl ether, polyethylene glycol laurate, sorbitan alkyl esters, etc.), cation type (dimethylaurylbenzyl ammonium chloride, laurylamine, stearyltrimethyl ammonium chloride, etc.) and amphoteric type (amino acids, betaine, etc.).

For purposes of improving properties of the preparation and enhancing the herbicidal effect, the herbicidal composition of the present invention may also contain high molecular compounds such as sodium alginate, carboxymethyl cellulose, carboxyvinyl polymer, gum arabic, hydroxypropylmethyl cellulose, etc. and auxiliary agents in combination.

The herbicidal composition of the present invention exhibits an excellent effect on weeds in field crops such as corn, sorghum, wheat, barley, oat, etc., as a high degree of selective herbicide without causing any phytotoxicities to crops by pre- or post-emergence treatment to the soil or the foliage of weeds. The herbicidal composition shows a high herbicidal effect not only against annual weeds but also against perennial weeds and is extremely useful as a high degree of selective herbicide without causing any phytotoxicities for paddy rice plants or lawns.

The herbicidal composition of the present invention also exhibits an excellent effect of controlling weeds in orchards or non-cultivated fields (factory areas, railways, roadsides, waterways, fallow grounds), etc., by treatment to the soil or to the foliage of weeds.

The herbicidal composition of the present invention is applied in an amount of about 0.1 to 2,000 g, preferably 1 to 200 g, per 10 ares. Where the composition is sprayed over the foliage of plant, the composition is diluted to about 1 to about 20,000 ppm, preferably 10 to 2,000 ppm and the diluted preparation is applied to the foliage.

5 The herbicidal composition of the present invention may also be used in combination with other herbicides. Examples of the conventional herbicides which can be used herein include diphenyl ether compounds, triazine compounds, phenoxyacetic acid compounds, carbamate compounds, thiolcarbamate compounds, acid anilide compounds, pyrazole compounds, phosphoric acid compounds, imidazolinone compounds, dinitroaniline compounds, bromoxinyl, ioxinyl, oxadiazon, etc.

10 Furthermore, the herbicidal composition of the present invention may also be used as admixture with insecticides, sterilizers, plant growth regulators, fertilizers, etc., if necessary.

Next, the present invention is described with reference to examples.

15 Firstly, a method for making formulations is specifically described by referring to formulation examples. In the following formulation examples, "part" refers to % by weight. As the triazine derivative (Compound A) and the sulfonylurea type herbicide (Compound B) compounds shown in Tables 1 and 2 were used, respectively.

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Table 1

Compound No.	Structural Formula	Name of Compound
A-1		2-amino-4-[1-(benzofuran-2'-yl)ethylamino]-6-(α -fluoro, α -methylethyl)-s-triazine
A-2		2-amino-4-[1-(benzofuran-2'-yl)ethylamino]-6(α -fluoroethyl)-s-triazine
A-3		2-amino-4-[1-(benzothio-phen-2'-yl)ethylamino]-6-(α -fluoro, α -methylethyl)-s-triazine
A-4		2-amino-4-[α -fluoro, α -methylethyl-6-(2,3,5'-dimethylphenoxy)-1-methylethylamino]-s-triazine
A-5		2-amino-4-(α -fluoro, α -methylethyl)-6-[2-(3'-fluorophenoxy)-1-methylethylamino]-s-triazine

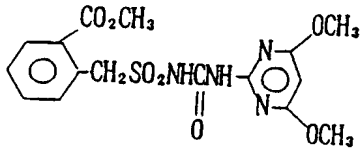
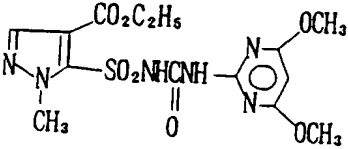
Table 1 (Continued)

Compound No.	Structural Formula	Name of Compound
A-6		2-amino-4-(α -chloro, α -methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine
A-7		2-amino-4-(α -fluoro, α -methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine

Table 2

Compound No.	Structural Formula	Name of Compound
B-1		methyl 2-[[[4-methoxy-6-methyl-1,3,5-triazin-2-yl]aminocarbonyl]-aminosulfonyl]benzoate
B-2		methyl 2-[[[4-methoxy-6-methyl-1,3,5-triazin-2-yl]aminocarbonyl]-aminosulfonyl]-thiophenecarboxylate
B-3		3-[(6-methoxy-4-methyl-1,3,5-triazin-2-yl)-1-[2-(2-chloroethoxy)-phenylsulfonyl]-urea
B-4		2-[3-(4,6-bis(difluoromethoxy)pyrimidin-2-yl)ureidosulfonyl]benzoic acid methyl ester
B-5		2-[(4,6-dimethoxypyrimidin-2-yl)carbamoylsulfamoyl]-N,N-dimethylnicotinamide
B-6		1-[(4,6-dimethoxypyrimidin-2-yl)-3-(ethylsulfonyl)-2-pyridinylsulfonyl]urea

Table 2 (Continued)

Compound No.	Structural Formula	Name of Compound
B-7		methyl 2-[[[(4,6-dimethoxy-pyrimidin-2-yl)amino-carbonyl]-aminosulfonyl]-methyl]benzoate
B-8		ethyl 5-(4,6-dimethoxy-pyrimidin-2-ylcarbamoylsulfamoyl)-1-methylpyrazol-4-carboxylate

Formulation Example 1 Wettable powders	
Compound A-1	5 parts
Compound B-1	15 parts
Diatomaceous earth	62 parts
White carbon	15 parts
Sodium alkylbenzenesulfonate	2 parts
Sodium lignin sulfonate	1 part

The foregoing components are blended with each other, uniformly kneaded and ground into powders to give 100 parts of wettable powders.

Formulation Example 2	Emulsifiable concentrate
Compound A-2	10 parts
Compound B-2	30 parts
Xylene	20 parts
Dimethylformamide	20 parts
Solpol 2806B (manufactured by Toho Chemical Industry, surfactant)	20 parts

The foregoing components are uniformly dissolved and blended to give 100 parts of emulsifiable concentrate.

Formulation Example 3 Dust	
Compound A-3	0.6 part
Compound B-6	1.4 parts
Diatomaceous earth	20 parts
Talc	78 parts

The foregoing components are blended with each other, uniformly kneaded and ground to give 100

parts of dusts.

Formulation Example 4 Granule	
Compound A-5	1 part
Compound B-7	3 parts
Bentonite	30 parts
Talc	63 parts
Sodium lignin sulfonate	3 parts

The foregoing components are thoroughly blended with each other, uniformly mixed and ground into powders. Water is added to the powders. After kneading them well, the blend is grained and dried to give 100 parts of granules.

Formulation Example 5 Flowable concentrate	
Compound A-7	10 parts
Compound B-4	15 parts
Methyl cellulose	0.3 part
Colloidal silica	1.5 parts
Sodium lignin sulfonate	1 part
Polyoxyethylene nonyl phenyl ether	2 parts
Water	70.2 parts

The foregoing components are thoroughly mixed and dispersed. The resulting slurry mixture is subjected to wet grinding to give 100 parts of stable flowable concentrate.

Formulation Example 6 Wettable powders

By uniformly blending 97 parts of clay (trademark: JIKURAITO, manufactured by JIKURAITO KOGYO) as a carrier, 1.5 parts of alkylaryl-sulfonate (trademark: NEOPELEX, manufactured by Kao Atlas-Co., Ltd.) as a surfactant, 1.5 parts of nonionic and anionic surfactant (trademark: Solpol 800A, manufactured by Toho Chemical Industry Co., Ltd.) and grinding into powders, a carrier for wettable powders was obtained.

By uniformly blending 90 parts of this carrier for wettable powders and 10 parts of the triazine derivative shown in Table 1 (Compounds A-1 through A-7) or 10 parts of the sulfonylurea type herbicide shown in Table 2 (Compounds B-1 to B-8) and grinding into powders, wettable powders were obtained.

Furthermore, the carrier for wettable powders containing the triazine derivative obtained above was blended with the carrier for wettable powders containing the sulfonylurea type herbicide in definite amounts (ratios as active ingredients), uniformly kneaded and ground into powders to give wettable powders.

Example 1 Test on post-emergence treatment

Wagner's pots of 1/2000 ares were filled with soil from upland fields and planted with weed seeds of *Galium aparine* L., *Velonica hedelifolia* and *Viola arvensis* and crop seeds of wheat, barley and oat. The seeds were then covered with soil and cultivated in a greenhouse. An aqueous suspension of a definite amount of the herbicide obtained in Formulation Example 6 was uniformly sprayed onto the foliage of 1.5 to 2.5 leaf stage of these weeds and 3 leaf stage of the crops at a spray volume corresponding to 100 liters/10 ares. Then, cultivation was performed in the greenhouse. After 20 days, crop injury and the herbicidal effect on the weeds were evaluated according to the criterion described below. The results are shown in Table 3.

(Criterion for assessment)

	Degree of herbicidal effect	Percent of weed control (herbicidal rate)
5	0	less than 5% (little effective)
10	1	5-20%
	2	20-40%
	3	40-70%
15	4	70-80%
	5	more than 90%
20		(almost all killed)

The herbicidal rate described above was determined according to the following equation by measuring the raw weight of weed on the ground in the treated group and the raw weight of weed on the ground in the untreated group.

25 Herbicidal rate (%)

$$30 \quad = \left(1 - \frac{\text{Weight of weed on the ground in the treated group}}{\text{Weight of weed on the ground in the untreated group}} \right) \times 100$$

35 Degree of crop injury

- 0 no injury to crops
- 1 little injury to crops
- 2 some injury to crops
- 40 3 injury to crops
- 4 serious injury to crops
- 5 almost all crops are withered to death

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Table 3

Active ingredient	Dosage (g/10a)	Herbicidal Effect			Crop Injury		
		Galium aparine L.	Veronica hedelifolia	Viola arvensis	Wheat	Barley	Sorghum
Triazine Derivative	A-1	10 5	2 1	3 2	3 2	0 0	0 0
	A-2	10 5	3 2	4 2	4 3	0 0	0 0
	A-3	10 5	3 1	3 2	3 2	0 0	0 0
	A-4	10 5	3 1	3 2	4 2	0 0	0 0
	A-5	10 5	3 2	4 3	4 3	0 0	0 0
	A-6	10 5	3 1	3 2	4 2	0 0	0 0
	A-7	10 5	4 2	4 2	4 3	0 0	0 0
Sulfonyl-urea Type Herbicide	B-1	0.6 0.3	2 1	3 2	2 1	0 0	0 0
	B-2	4 2	2 1	2 1	3 2	0 0	0 0
	B-3	1 0.5	3 2	3 1	3 2	0 0	0 0

Table 3 (Continued)

Triazine Derivative	Sulfonylurea Type Herbicide	Herbicidal Effect			Crop Injury		
		Galium aparine L.	Veronica hedelifolia	Viola arvensis	Wheat	Barley	Sorghum
Kind Dosage (g/10a)	Kind Dosage (g/10a)						
A-1 10 10 5 5	B-1 0.6 0.3 0.6 0.3	5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
A-2 10 10 5 5	B-1 0.6 0.3 0.6 0.3	5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
A-2 10 10 5 5	B-2 4 2 4 2	5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
A-2 10 10 5 5	B-3 1 0.5 1 0.5	5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
A-3 10 10 5 5	B-2 4 2 4 2	5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
A-4 10 10 5 5	B-3 1 0.5 1 0.5	5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
A-5 10 10 5 5	B-1 0.6 0.3 0.6 0.3	5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
A-5 10 10 5 5	B-2 4 2 4 2	5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
A-5 10 10 5 5	B-3 1 0.5 1 0.5	5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
A-6 10 10 5 5	B-2 4 2 4 2	5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0
		5	5	5	0	0	0

Table 3 (Continued)

Triazine Derivative		Sulfonylurea Type Herbicide		Herbicidal Effect			Crop Injury		
Kind	Dosage (g/10a)	Kind	Dosage (g/10a)	Galium aparine L.	Veronica hedelifolia	Viola arvensis	Wheat	Barley	Sorghum
A-7	10	B-1	0.6	5	5	5	0	0	0
	10		0.3	5	5	5	0	0	0
	5		0.6	5	5	5	0	0	0
	5		0.3	5	5	5	0	0	0
A-7	10	B-2	4	5	5	5	0	0	0
	10		2	5	5	5	0	0	0
	5		4	5	5	5	0	0	0
	5		2	5	5	5	0	0	0
A-7	10	B-3	1	5	5	5	0	0	0
	10		0.5	5	5	5	0	0	0
	5		1	5	5	5	0	0	0
	5		0.5	5	5	5	0	0	0

Some data were extracted from the results shown in Table 3 and the synergistic effect of the triazine derivative and the sulfonylurea type herbicide was examined on Galium aparine L., and Viola arvensis according to the following method.

$$Q E = Q a + Q b - \frac{Q a \cdot Q b}{100}$$

Qa : found data (%) of herbicidal rate when treated at a dosage corresponding to a g/10 ares using the triazine derivative alone as active ingredient

Qb : found data (%) of herbicidal rate when treated at a dosage corresponding to b g/10 ares using the sulfonylurea derivative alone as active ingredient

QE : expected value

[Limpel, L.E., P.H. Schuldt and D. Lamont, Proc. NEWCC, 16, 48-53 (1962)]

Herein, when the found data (herbicidal rate) of the herbicidal obtained by mixing the triazine derivative and the sulfonylurea type herbicide is larger than QE, it can be said that the herbicidal activity is synergistic. The results are shown in Table 4.

Table 4

Triazine Derivative		Sulfonylurea Type Herbicide		Herbicidal Effect			
Kind	Dosage (g/10a)	Kind	Dosage (g/10a)	Percent control of Galium aparine L. (%)	Expected Value (Q _e) (%)	Percent control of Viola arvensis (%)	Expected Value (Q _e) (%)
-	-	B-1	0.6	38	-	37	-
-	-	B-2	4	36	-	48	-
-	-	B-3	1	52	-	54	-
A-1	10	-	-	39	-	48	-
A-1	10	B-1	0.6	94	62	97	67
A-2	5	-	-	38	-	64	-
A-2	5	B-1	0.6	95	62	98	77
A-2	5	-	-	38	-	64	-
A-2	5	B-2	0.4	94	60	98	81
A-2	5	-	-	38	-	64	-
A-2	5	B-3	0.1	96	70	98	83
A-3	10	-	-	54	-	56	-
A-3	10	B-2	4	94	71	97	77
A-4	10	-	-	58	-	70	-
A-4	10	B-3	1	98	80	100	86
A-5	5	-	-	36	-	68	-
A-5	5	B-1	0.6	96	60	99	80
A-5	5	-	-	36	-	68	-
A-5	5	B-2	4	95	59	100	83
A-5	5	-	-	36	-	68	-
A-5	5	B-3	1	97	69	100	85
A-6	10	-	-	62	-	72	-
A-6	10	B-2	4	99	76	100	85
A-7	5	-	-	40	-	58	-
A-7	5	B-1	0.6	98	63	97	74
A-7	5	-	-	40	-	58	-
A-7	5	B-2	4	96	62	98	78
A-7	5	-	-	40	-	58	-
A-7	5	B-3	1	97	71	99	81

Example 2 Test on post-emergence treatment

Wagner's pots of 1/2000 ares were filled with soil from upland fields and planted with weed seeds of *Digitaria sanguinalis*, *Abutilon theophrasti* and *Ipomoea purpurea* and crop seeds of corn and sorghum. The seeds were then covered with soil and cultivated in a greenhouse. An aqueous suspension of a definite amount of the herbicide obtained in Formulation Example 6 was uniformly sprayed onto the foliage of 2 to 3 leaf stage of these weeds and 3 leaf stage of the crops at a spray volume corresponding to 100 liters/10 ares. Then, cultivation was performed in the greenhouse. After 20 days, crop injury and the herbicidal effect on the weeds were evaluated according to the same criterion described in Example 1. The results are shown in Table 5.

Table 5

Active ingredient		Dosage (g/10a)	Herbicidal Effect			Crop Injury	
			Digitaria sanguinalis	Abutilon theophrasti	Ipomoea purpurea	Corn	Sorghum
Triazine Derivative	A-1	10 5	3 1	3 1	4 2	0 0	0 0
	A-2	10 5	3 2	4 2	4 2	0 0	0 0
	A-3	10 5	2 1	3 2	4 2	0 0	0 0
	A-4	10 5	2 1	3 2	4 3	0 0	0 0
	A-5	10 5	3 2	4 3	5 4	0 0	0 0
	A-6	10 5	3 1	3 2	5 3	0 0	0 0
	A-7	10 5	3 2	4 3	5 4	0 0	0 0
Sulfonylurea Type Herbicide	B-4	1 0.5	4 3	2 1	2 1	0 0	0 0
	B-5	0.6 0.3	4 2	3 2	2 1	0 0	0 0
	B-6	4 2	3 2	2 1	3 2	0 0	0 0

Table 5 (Continued)

Triazine Derivative	Kind Dosage (g/10a)	Sulfonylurea Type Herbicide	Kind Dosage (g/10a)	Herbicidal Effect			Crop Injury	
				Digitaria sanguinalis	Abutilon theophrasti	Ipomoea purpurea	Corn	Sorghum
A-1	10	B-4	1	5	5	5	0	0
	10		0.5	5	5	5	0	0
	5		1	5	5	5	0	0
	5		0.5	5	5	5	0	0
A-2	10	B-4	1	5	5	5	0	0
	10		0.5	5	5	5	0	0
	5		1	5	5	5	0	0
	5		0.5	5	5	5	0	0
A-2	10	B-5	0.6	5	5	5	0	0
	10		0.3	5	5	5	0	0
	5		0.6	5	5	5	0	0
	5		0.3	5	5	5	0	0
A-2	10	B-6	4	5	5	5	0	0
	10		2	5	5	5	0	0
	5		4	5	5	5	0	0
	5		2	5	5	5	0	0
A-3	10	B-5	0.6	5	5	5	0	0
	10		0.3	5	5	5	0	0
	5		0.6	5	5	5	0	0
	5		0.3	5	5	5	0	0
A-4	10	B-6	4	5	5	5	0	0
	10		2	5	5	5	0	0
	5		4	5	5	5	0	0
	5		2	5	5	5	0	0
A-5	10	B-4	1	5	5	5	0	0
	10		0.5	5	5	5	0	0
	5		1	5	5	5	0	0
	5		0.5	5	5	5	0	0
A-5	10	B-5	0.6	5	5	5	0	0
	10		0.3	5	5	5	0	0
	5		0.6	5	5	5	0	0
	5		0.3	5	5	5	0	0
A-5	10	B-6	4	5	5	5	0	0
	10		2	5	5	5	0	0
	5		4	5	5	5	0	0
	5		2	5	5	5	0	0
A-6	10	B-5	0.6	5	5	5	0	0
	10		0.3	5	5	5	0	0
	5		0.6	5	5	5	0	0
	5		0.3	5	5	5	0	0

Table 5 (Continued)

Triazine Derivative		Sulfonylurea Type Herbicide		Herbicidal Effect			Crop Injury	
Kind	Dosage (g/10a)	Kind	Dosage (g/10a)	Digitaria sanguinalis	Abutilon theophrasti	Ipomoea purpurea	Corn	Sorghum
A-7	10	B-4	1	5	5	5	0	0
	10		0.5	5	5	5	0	0
	5		1	5	5	5	0	0
	5		0.5	5	5	5	0	0
A-7	10	B-5	0.6	5	5	5	0	0
	10		0.3	5	5	5	0	0
	5		0.6	5	5	5	0	0
	5		0.3	5	5	5	0	0
A-7	10	B-6	4	5	5	5	0	0
	10		2	5	5	5	0	0
	5		4	5	5	5	0	0
	5		2	5	5	5	0	0

Example 3 Paddy field test (post-emergence treatment test)

Pots of 1/2000 are were filled with soil from paddy fields and seeded with seeds from Echinochloa crus-galli. Then, water was filled to a depth of 3 cm.

Thereafter when Echinochloa crus-galli reached the 1.5-leaf stage, a definite amount of a dilution of the herbicide obtained in Formulation Example 6 was dropped on the water surface. Then, the weeds were allowed to stand in a greenhouse. Twenty days after the treatment, the herbicidal effect on the weeds evaluated according to the criterion of Example 1. The results are shown in Table 6.

Table 6

Active ingredient		Dosage (g/10a)	Herbicidal Effect for Echinochloa crus-galli
Triazine Derivative	A-1	10 5	4 2
	A-2	10 5	4 2
	A-3	10 5	3 2
	A-4	10 5	3 2
	A-5	10 5	4 3
	A-6	10 5	3 2
	A-7	10 5	4 3
Sulfonylurea Type Herbicide	B-7	4 2	2 1
	B-8	1 0.5	3 2

Table 6 (Continued)

Triazine Derivative		Sulfonylurea Type Herbicide		Herbicidal Effect for Echinochloa crus-galli
Kind	Dosage (g/10a)	Kind	Dosage (g/10a)	
A-1	10	B-7	4	5
	10		2	5
	5		4	5
	5		2	5
A-1	10	B-8	1	5
	10		0.5	5
	5		1	5
	5		0.5	5
A-2	10	B-7	4	5
	10		2	5
	5		4	5
	5		2	5
A-2	10	B-8	1	5
	10		0.5	5
	5		1	5
	5		0.5	5
A-3	10	B-7	4	5
	10		2	5
	5		4	5
	5		2	5
A-3	10	B-8	1	5
	10		0.5	5
	5		1	5
	5		0.5	5
A-4	10	B-7	4	5
	10		2	5
	5		4	5
	5		2	5
A-4	10	B-8	1	5
	10		0.5	5
	5		1	5
	5		0.5	5
A-5	10	B-7	4	5
	10		2	5
	5		4	5
	5		2	5
A-5	10	B-8	1	5
	10		0.5	5
	5		1	5
	5		0.5	5

Table 6 (Continued)

Triazine Derivative		Sulfonylurea Type Herbicide		Herbicidal Effect for Echinochloa crus-galli
Kind	Dosage (g/10a)	Kind	Dosage (g/10a)	
A-6	10	B-7	4	5
	10		2	5
	5		4	5
	5		2	5
A-6	10	B-8	1	5
	10		0.5	5
	5		1	5
	5		0.5	5
A-7	10	B-7	4	5
	10		2	5
	5		4	5
	5		2	5
A-7	10	B-8	1	5
	10		0.5	5
	5		1	5
	5		0.5	5

Example 4 Field test (pre-emergence treatment test)

Test zone having each plot of 2 m² were prepared and weed seeds of Galium aparine L., Stellaria media, Viola arvensis, Matricaria inodora, Veronica hedelifolia, Papaver rhoeas and Aphanes arvensis and crop seeds of wheat and barley were simultaneously planted.

At the pre-emergence timing of wheat, barley and weeds, a given amount of a dilution of the herbicide obtained in Formulation Example 6 was uniformly sprayed over the soil surface at a spray volume corresponding to 20 liters/10 ares. The test was carried out by 3 replications.

The weeds on the ground which survived 60 days after spraying of the chemical were cut out and their raw weight were measured. According to the following equation, a weed controlling rate was determined as an average of the 3 replicates.

Percent of weed control (%) =

$$\left(1 - \frac{\text{Weight of survived weed on the ground in the treated plot}}{\text{Weight of survived weed on the ground in the untreated plot}}\right) \times 100$$

With respect to wheat and barley, their raw weights on the ground were measured also as in weeds and the degree of crop injury (inhibition rate) was determined. The results are shown in Table 7.

Table 7

Active ingredient	A-2 + B-1	A-2 + B-1	A-7 + B-1	A-7 + B-1
Dosage(g/10a)	20+0.6	10+0.6	20+0.6	10+0.6
Percent of Weed Control(%)				
Galium aparine L.	100	100	100	100
Stellaria media	100	100	100	100
Viola arvensis	100	100	100	100
Matricaria inodora	100	100	100	100
Veronica hedelifolia	100	100	100	100
Papaver rhoeas	100	100	100	100
Aphanes arvensis	100	100	100	100
Crop Injury				
Wheat	0	0	0	0
Barley	0	0	0	0

-----Example 5: Field-test (post-emergence treatment-test)-----

Test zones having each plot of 2 m² were prepared and weed seeds of Galium aparine L., Stellaria media, Viola arvensis, Matricaria inodora, Veronica hedelifolia, Papaver rhoeas and Aphanes arvensis and crop seeds of wheat and barley were simultaneously planted.

When weeds grew at the 2-3 leaf stage and wheat and barley reached the 3-leaf stage, a given amount of a dilution of the herbicide obtained in Formulation Example 6 was uniformly sprayed onto the foliage at a spray volume corresponding to 20 liters/10 ares.

The percent of weed control and the degree of crop injury were determined 30 days after spraying the chemical in a manner similar to Example 4. The results are shown in Table 8.

Table 8

Active ingredient	A-2+B-1	A-2+B-1	A-7+B-1	A-7+B-1	A-2+B-2	A-2+B-2	A-7+B-2	A-7+B-2
Dosage(g/10a)	20+0.6	10+0.6	20+0.6	10+0.6	20+4	10+4	20+4	10+4
Percent of Weed Control(%)								
Galium aparine L.	100	100	100	100	100	100	100	100
Stellaria media	100	100	100	100	100	100	100	100
Viola arvensis	100	100	100	100	100	100	100	100
Matricaria inodora	100	100	100	100	100	100	100	100
Veronica hedelifolia	100	100	100	100	100	100	100	100
Papaver rhoeas	100	100	100	100	100	100	100	100
Aphanes arvensis	100	100	100	100	100	100	100	100
Crop Injury								
Wheat	0	0	0	0	0	0	0	0
Barley	0	0	0	0	0	0	0	0

Example 6 Field test (post-emergence treatment test)

Test zones having each plot of 2 m² were prepared and weed seeds of Digitaria sanguinalis, Xanthium strumarium, Ipomoea purpurea, Abutilon theophrasti, Portulaca oleracea, Solanum nigrum, Cassia obtusifolia L., and Amaranthus retroflexus and crop seeds of corn and sorghum were simultaneously planted.

When weeds grew at the 2-3 leaf stage and corn and sorghum reached the 3-leaf stage, a given amount of a dilution of the herbicide obtained in Formulation Example 6 was uniformly sprayed onto the foliage at a spray volume corresponding to 20 liters/10 ares. The percent of weed control and the degree of crop injury were determined 30 days after spraying the chemical in a manner similar to Example 4. The results are shown in Table 9.

Table 9

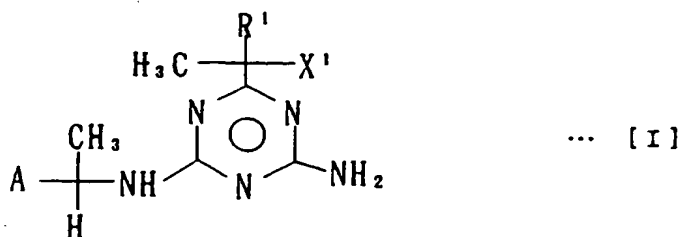
Active ingredient	A-2 + B-4	A-2 + B-4	A-7 + B-4	A-7 + B-4
Dosage(g/10a)	20+1	10+1	20+1	10+1
Percent of Weed Control(%)				
<i>Digitaria sanguinalis</i>	100	100	100	100
<i>Xanthium strumarium</i>	100	100	100	100
<i>Ipomoea purpurea</i>	100	100	100	100
<i>Abutilon theophrasti</i>	100	100	100	100
<i>Portulaca oleracea</i>	100	100	100	100
<i>Solanum nigrum</i>	100	100	100	100
<i>Cassia obtusifolia</i> L.	100	100	100	100
<i>Amaranthus retroflexus</i>	100	100	100	100
Crop Injury				
Corn	0	0	0	0
Sorghum	0	0	0	0

By the synergistic effect of the triazine derivative and sulfonylurea type herbicide as active ingredients, the herbicidal composition of the present invention show a high herbicidal effect at a low dosage and also have a wide range of herbicidal spectrum. Further when the composition is used as herbicide for field crops, the composition has flexibility of treatment to exhibit effectiveness, as compared to in conventional herbicides for field crops. The composition also shows a high herbicidal activity even against troublesome weeds both by treatment to the soil at the pre- or post-emergence of weeds and by treatment to the foliage at the post-emergence of weeds. In addition, no crop injury is caused. In particular, the effect is markedly high in treatment to the soil or foliage treatment in fields where Gramineae crops grow. Further, when the present herbicide is used as a herbicide for paddy rice, it shows excellent herbicidal effect not only against annual weeds but also against perennial weeds.

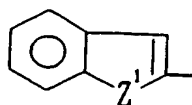
While the invention has been described in detail and with reference to specific embodiments thereof, it is apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and the scope of the present invention.

Claims

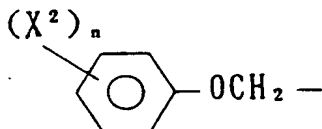
1. A herbicidal composition comprising as active ingredient a triazine derivative represented by general formula [I]:



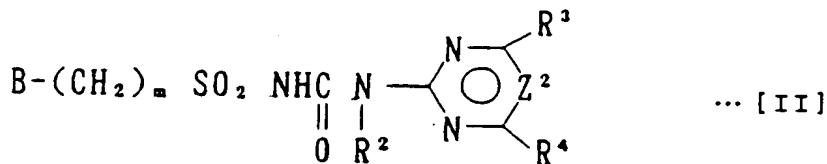
wherein A represents



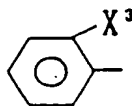
wherein Z represents oxygen atom or sulfur atom, or



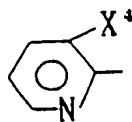
wherein X^2 represents methyl group or fluorine atom and n represents 0 or an integer of 1 or 2; R^1 represents hydrogen atom or methyl group; and X^1 represents fluorine atom or chlorine atom and a sulfonylurea type herbicide represented by general formula [II]:



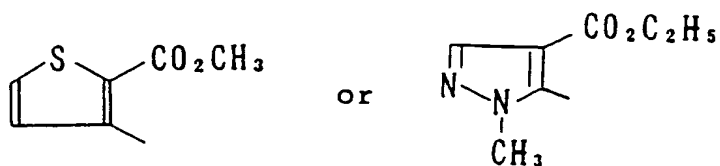
wherein B represents



wherein X^3 represents a chlorine atom, CO_2CH_3 , $CO_2C_2H_5$ or OCH_2CH_2Cl ,



wherein X^4 represents $CON(CH_3)_2$ or $CO_2C_2H_5$,



R² represents a hydrogen atom or methyl group, R³ and R⁴ each represents methyl group, OCH₃ or OCHF₂, provided that R³ and R⁴ may be the same or different; Z² represents CH or a nitrogen atom, and m is 0 or 1.

- 5 2. The herbicidal composition as claimed in claim 1, wherein the triazine derivative represented by general formula [I] is a triazine derivative selected from the group consisting of 2-amino-4-[1-(benzofuran-2'-yl)ethylamino]-6-(α -fluoro, α -methylethyl)-s-triazine, 2-amino-4-[1-(benzofuran-2'-yl)ethylamino]-6-(α -fluoroethyl)-s-triazine, 2-amino-4-[1-(benzothiophen-2'-yl)ethylamino]-6-(α -fluoro, α -methylethyl)-s-triazine, 2-amino-4-(α -fluoro, α -methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine, 2-amino-4-(α -fluoro, α -methylethyl)-6-[2-(3'fluorophenoxy)-1-methylethylamino]-s-triazine, 2-amino-4-(α -chloro, α -methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine and 2-amino-4-(α -fluoro, α -methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine.
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- 15 3. The herbicidal composition as claimed in claim 1, wherein the sulfonylurea type herbicide represented by general formula [II] is a sulfonylurea type herbicide selected from the group consisting of 2-chloro-N-[4-methoxy-6-methyl-1,3,5-triazin-2-yl]-aminocarbonyl]benzenesulfonamide, methyl 2-[[4-methoxy-6-methyl-1,3,5-triazin-2-yl]-aminocarbonyl]-aminosulfonyl]benzoate, methyl 2-[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-3-methylureidosulfonyl]benzoate, methyl 3-[[4-methoxy-6-methyl-1,3,5-triazin-2-yl]-aminocarbonyl]-aminosulfonyl]-2-thiophenecarboxylate, 3-(6-methoxy-4-methyl-1,3,5-triazin-2-yl)-1-[2-(2-chloroethoxy)-phenylsulfonyl]urea, methyl 2-[[4,6-dimethyl-pyrimidin-2-yl]aminocarbonyl]-aminosulfonyl]benzoate, 2-[3-(4,6-bis(difluoromethoxy)-pyrimidin-2-yl)-ureidosulfonyl]benzoic acid methyl ester, 2-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-N,N-dimethylnicotinamide, 1-(4,6-dimethoxypyrimidin-2-yl)-3-(ethylsulfonyl)-2-pyridinylsulfonylurea, methyl 2-[[[4,6-dimethoxypyrimidin-2-yl]aminocarbonyl]-aminosulfonyl]methyl]benzoate and ethyl 5-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-1-methylpyrazol-4-carboxylate.
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European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 11 3287

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 932 998 (T. TAKEMATSU et al.) * Column 18, lines 40-51 *	1-3	A 01 N 43/68 // (A 01 N 43/68 A 01 N 47:36)
A,P	EP-A-0 411 153 (IDEMITSU KOSAN) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A 01 N
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 24 September 91	Examiner DECORTE D.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</div> <div>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document</div>			

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